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FATE OF TRACE CONSTITUENTS OF COAL DURING GASIFICATION

INSTITUTE OF GAS TECHNOLOGY

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FATE OF TRACE CONSTITUENTS OF COAL DURING GASIFICATION

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Coal Gasification
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Arsenic
Beryllium
Cadmium
Chromium
Lead (metal)
Mercury (metal)
Nickel
Selenium
Tellurium
Vanadium

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FATE OF TRACE CONSTITUENTS OF COAL DURING GASIFICATION

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ABSTRACT

This study was initiated by the Environmental Protection Agency to investigate the fate of trace elements of coal during the coal gasification process for the production of pipeline-quality gas. The ultimate goal of the investigation is to provide the necessary information that will enable environmentally sound operation of future commercial-scale coal gasification plants.

The present report is the result of a 6-month preliminary effort to set up laboratory analytical methods and to analyze for antimony, arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, tellurium, and vanadium in a bituminous raw coal and its solid residues from a bench-scale coal gasification unit at the Institute of Gas Technology. The samples selected are representative of the solid effluents from the pretreatment, hydrogasification, and electrothermal stages of the IGT HYGAS pilot plant.

The data obtained thus far indicate substantial removal of arsenic, cadmium, lead, mercury, selenium, and tellurium from coal during the gasification process. However, since these results are based on a limited number of samples, further analysis of a larger number of samples is required before any firm conclusions can be drawn.

This report is submitted by the Institute of Gas Technology in fulfillment of Contract Number 68-02-0277 under the partial sponsorship of the Environmental Protection Agency. Work was completed as of November 1972.

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INTRODUCTION

With the increasing demand for energy and the growing snortage of petroleum oil and natural gas in the United States, a great impetus has been given to the study of conversion of our large coal deposits to pipeline-quality gas via coal gasification processes. The Institute of Gas Technology estimates that by 1990 we will witness the construction and operation of some 40 large-scale coal gasification plants, each capable of processing approximately 6 million tons of coal annually, with an estimated total yearly production of 2.7 trillion cubic feet of gas. This projected large-scale consumption of coal necessitates a thorough investigation of its impact on the environment, since trace quantities of toxic elements such as antimony, beryllium, mercury, and selenium are known to exist in some U. S. coal deposits. A knowledge of the level of these potentially hazardous pollutants and their fate during the coal gasification process is necessary for such an investigation.

The Institute of Gas Technology (IGT) has been engaged in gasification research since 1942. In 1964 it was awarded the HYGAS Process Research contract under the joint sponsorship of the U. S. Office of Coal Research (OCR) and American Gas Association (A. G. A.). The project consisted of the design, construction, and operation of a large pilot facility with a daily capacity of 75 tons of coal and the production of 1.5 million cubic feet of pipeline-quality gas. This plant was completed in May 1971 at a cost of $10 million and has been intermittently operational since October 1971.

In May of 1972 IGT was awarded a 6-month research contract by the Environmental Protection Agency (EPA Contract No. 68-02-0277) to set up and measure the concentration of 11 trace elements in a Pittsburgh No. 8 coal sample and its 5 solid residues, representing the coal input and output of each of the three stages of the HYGAS pilot plant, as shown in Figure 1.

Since the HYGAS plant was not fully operational at that time, it was decided to draw upon IGT's large collection of coal and char samples accumulated over several years of gasification research during bench-scale development of the HYGAS plant.

The initial 2-month period was devoted to study of the effect of ashing temperature on the recovery of some of the more volatile trace elements. The low-temperature plasma ashing machine was studied intensively for

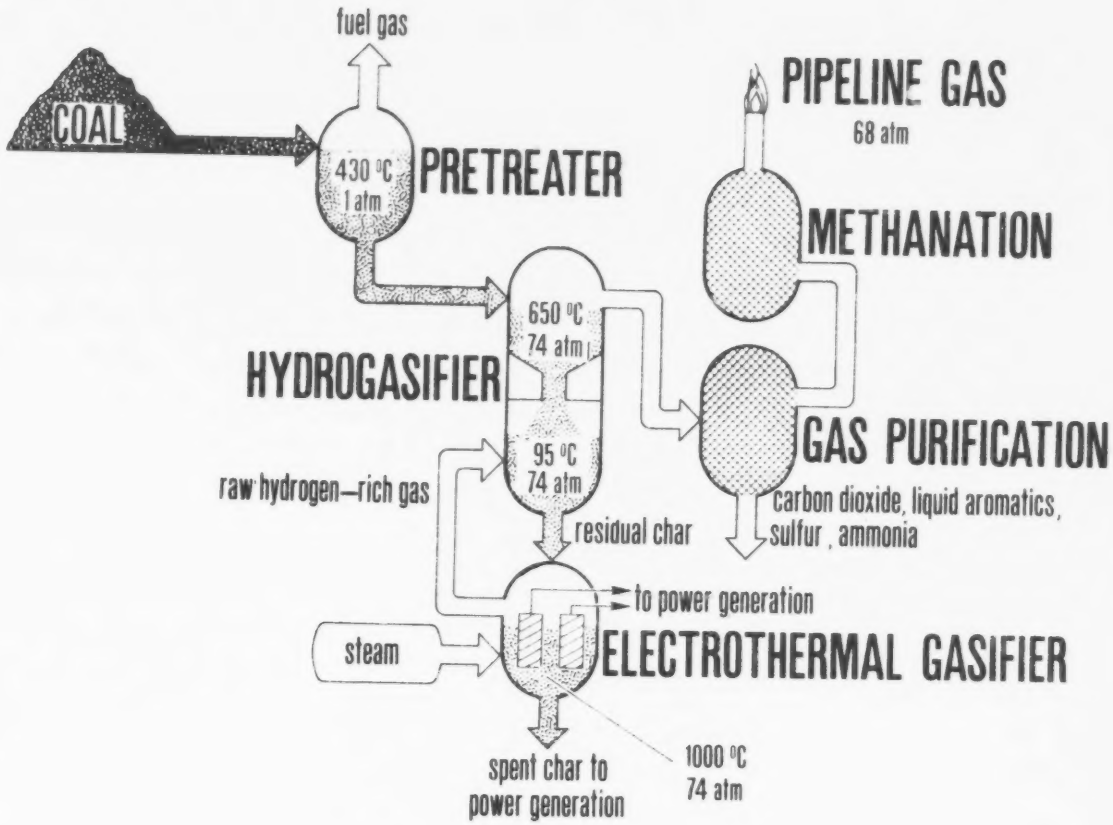

Figure 1. IGT HYGAS PROCESS FOR ELECTROTHERMAL GASIFICATION, SHOWING PRETREATMENT, HYDROGASIFICATION, AND ELECTROTHERMAL STAGES

its application to the ashing of coal samples because some more volatile elements were lost during the high-temperature ashing process – even at 550 °C.

The following 4-month period consisted of the laboratory setup and analysis of beryllium, chromium, lead, nickel, vanadium, antimony, arsenic, cadmium, mercury, selenium, and tellurium in the No. 8 coal sample and residues. An effort was made to use the atomic absorption spectrophotometer for these analyses. The microsampling kit, the graphite furnace, and the mercury analyzer assemblies on the conventional atomic absorption spectrophotometer (AAS) made it possible to determine these 11 elements with a precision comparable to other analytical methods.

CHAPTER I. EXPERIMENTAL

A. IDENTIFICATION OF INSTRUMENTATION

The International Plasma low-temperature asher (LTA) IPC Model 1005B was used throughout this work for ashing of coal.

The Perkin-Elmer Model 303 double-beam atomic absorption spectrophotometer with a background compensator installed internally, a nebulizer burner assembly, and a Sargeant TR 10-inch strip-chart recorder was used in most of the work. The Perkin-Elmer microsampling assembly was used for part of the work, and the Perkin-Elmer mercury analysis system 303-0832 was used for mercury determination.

B. SAMPLE SELECTION

The six coal samples selected for this work were taken from the following series of IGT small-scale gasification runs.

1. Pittsburgh No. 8 Seam bituminous coal used as feed in the pretreatment Run No. FP-147 plus the partially gasified pretreated coal residues of this run designated as F-FP-147 and R-FP-147, respectively.

2. Pretreated coal from Run No. FP-147, which was used as feed in the hydrogasification Run No. OH-9, together with the residues of this run, which are designated as F-OH-9 and R-OH-9, respectively.

3. Hydrogasified char from Run No. OH-9, which was used as feed in the electrothermal gasification Run No. EGO-37, and the spent chars from this run, which are, respectively, designated as F-EGO-37 and R-EGO-37.

C. PROXIMATE AND ULTIMATE ANALYSES

Proximate and ultimate analyses were performed on these six samples in order to present some qualitative properties which would aid in a more intelligent choice of samples for further analyses.

D. ASHING OF COAL

In low-temperature ashing of coal, the raw coal was utilized to show the relationship between the radio frequency (RF) power input and the sample temperature. The ashing rate was studied as a function of coal particle size using duplicates of the six samples. The coal samples were

ashed for 30 hours in the low-temperature asher, using raking and mixing to achieve a new ashing surface every 2 hours.

In high-temperature ashing, the coal samples were ashed overnight in a muffle furnace, keeping the temperature under 550 °C.

To measure loss of volatile elements in high-temperature ashing, six samples were ground to 80-mesh size, and each was taken in 5-gram quadruplicates for ashing. The first pair of samples were ashed at 120°C (in the LTA) and the second pair were ashed at 550°C in a muffle furnace. The ashed materials were then reacted with mineral acids, and the resulting solution was analyzed by atomic absorption spectroscopy.

E. ACID DISSOLUTION OF COAL ASH

1. General Considerations

The sample preparations were different for different elements. The widely used perchloric-hydrofluoric acid dissolution[1,2,3] for coal ash is suitable, with minor modifications, for the determination of beryllium, cadmium, chromium, nickel, lead, and vanadium. With low-temperature ashing, the final products still contain about 1% carbon. It is, therefore, necessary to treat the sample with a small amount of concentrated nitric acid before adding hydrofluoric acid. Arsenic, antimony, selenium, and tellurium might be volatilized under perchloric-hydrofluoric acid dissolution. Therefore, sulfuric acid and nitric acid treatments were used for these elements.[4]

For mercury determination, even the low-temperature ashing process results in loss of mercury.[5,6] It is easier to combust the coal sample and collect the mercury from the vapor phase[7-10] either by gold amalgamation or by absorbent solution than it is to prevent loss of mercury during ashing.

2. Acid Dissolution

Methods for acid dissolution of coal ash differ according to the trace elements being investigated.

a. For determination of beryllium, cadmium, nickel, lead, and vanadium, 0.500 gram of coal ash is placed in a platinum crucible with 5 ml concentrated nitric acid and heated on a hot plate until the brown fumes disappear. The residue is cooled, 3 ml of concentrated perchloric acid added, and heated again until white fumes appear. When the

mixture has cooled, 10 ml 49% hydrofluoric acid is added, and heat applied until white fumes appear. After cooling and the addition of 10 ml deionized water, the solution is heated to a boil, cooled, and filtered through Whatman No. 42 paper into a 50-ml volumetric flask. The paper and residue are washed thoroughly, then 50 mg of potassium (as potassium chloride) is added before making up the solution to volume.

b. For determination of arsenic, antimony, selenium, and tellurium, 0.500 gram of coal ash is placed in a beaker with 4 ml of concentrated sulfuric acid and 10 ml of concentrated nitric acid and heated on a hot plate until white fumes appear. After the residue has cooled, 5 ml of deionized water is added and the mixture heated until white fumes again appear. After cooling and addition of 30 ml of deionized water, the solution is heated to a boil, cooled, and filtered through Whatman No. 42 paper into a 50-ml volumetric flask. The paper and residue are washed thoroughly and the solution made to volume.

F. SAMPLE PREPARATION FOR MERCURY ANALYSIS

This procedure consists of the combustion of the coal sample in a stream of oxygen and the recovery of mercury vapors from the combustion products of the sample by the use of a suitable absorbing solution for the subsequent analysis of the resulting solution by a nonflame atomic absorption method.

The combustion apparatus is assembled according to the specifications of ASTM D271 (Ultimate Analysis of Coal). The equipment consists of a 97-cm-long Vycor tube with a 1.9-cm inside diameter having one reduced end for rubber tubing connection. The Vycor tube is packed with a 20-cm section of silver wire followed by a 30-cm section of copper oxide. Copper gauze plugs are conveniently used to separate the packings and are also placed at each end of the packings to prevent their displacement.

Three separate tube furnaces are used to heat the different sections of the combustion tube at different temperatures. The silver wire section is covered by a 23-cm-long furnace maintained at 450°-500°C, while the copper oxide section is heated by a 33-cm furnace kept at 800°-850°C. Finally, the sample section is heated with a 13-cm movable furnace which can rapidly attain a temperature of 900°C during the run.

Two 125-ml gas-washing bottles with fritted cylinders are connected in series to the exit end of the combustion tube. Each bottle is charged with 50 ml

of an absorbing solution containing 1% potassium permanganate in 0.1N sulfuric acid solution.

To make a run, a 0.5-gram sample of coal is weighed in a porcelain boat and placed into the combustion tube. The oxygen flow rate is set at 75 ml/min, and the sample furnace is fully turned on and allowed to cover the boat in 20 minutes. After an additional 20 minutes combustion time, the sample furnace is turned off and pulled back to its original position. At the end of this period the absorbing solutions are quantitatively transferred to a 200-ml volumetric flask and the volume brought up to mark; the solutions are saved for further analysis.

G. DETERMINATION OF INDIVIDUAL ELEMENTS

1. Chromium

The chromium line 357.8 nm was used in this work. The determination of chromium was done by direct aspiration of the sample solution into an air-acetylene flame. The sensitivity of the chromium in the flame is highly dependent on the richness of the fuel. A rather fuel-rich flame was used because it gave best sensitivity.

A series of standard solutions containing 0-5 ppm of chromium was prepared. The concentrations of chromium in the sample solutions were calculated from the standard curve.

2. Nickel

The nickel line 232.0 nm was used in this work. The determination of nickel by direct aspiration of the sample solution into the air-acetylene flame was reasonably good with scale expansion.

When 10X scale expansion is used, it is necessary to set the slit width to 4 (1 mm). The sensitivity would be reduced to about half if the slit width were set on 3 (0.3 mm). The width of 4 will stabilize the background better. A series of standard solutions was prepared containing 0-5 ppm of nickel.

3. Vanadium

Vanadium line 318.4 nm was used in this work, with a nitrous oxide-acetylene flame. Direct aspiration of the sample solution into the flame required 10X scale expansion.

An attempt was made to extract vanadium into the organic solvent by use of ammonium pyrrolidine carbodithioate (APCD) in order to give a larger signal size. The extraction of vanadium by chelating it with APCD followed by methyl isobutyl ketone (MIBK) extraction has been found quite satisfactory with the vanadium standard solutions. However, it did not work for the sample solutions due to interference from the large amounts of the iron existing in the sample. Separation of iron by ammonium thiocyanade extraction or hydroxide-ion precipitation would remove vanadium at the same time.

Therefore, the vanadium was determined by direct aspiration of the sample solution into the nitrous oxide-acetylene flame. The sensitivity of the measurement is strongly dependent on flame condition. The highest sensitivity is attained when the red-feather zone is about 1 cm high. The relative standard deviation was about 9% at the level of 2 ppm vanadium in the sample solution with scale expansion at 10X.

4. Beryllium

Beryllium line 234.9 nm was used. In the first half of the work beryllium was determined by direct aspiration of the sample solution into the nitrous oxide flame, and in the second half of the work it was determined by graphite furnace.

The determination of beryllium by a nitrous oxide-acetylene flame is not very good at its concentration in this coal. A rather fuel-rich flame is required to get the highest sensitivity. One percent oxine was added to the sample solution to offset the interference caused by the high aluminum in the sample. The 10X scale expansion was used during the measurement.

In the second half of the work, the beryllium was again determined by the graphite furnace technique. The sample solution was diluted tenfold and a series of standard solutions containing 0 to 0.005 ppm of beryllium was prepared. Operating conditions of the graphite furnace are given in Table 1.

Table 1. GRAPHITE FURNACE CONDITIONS FOR BERYLLIUM

	Time, s	Temperature, °C
Drying	50	150
Ashing	50	400
Atomizing	4	2600

5. Lead

Lead line 283.3 nm was used. Lead was first determined by APCD-MIBK extraction followed by air-acetylene flame atomic absorption. The iron was separated prior to APCD-MIBK extraction by adding ammonium thiocyanade and shaking with isoamyl alcohol or tributyl phosphate (TBP).

In APCD-MIBK extraction of lead, the pH of the sample solution was adjusted to 3.5 ± 0.1 before adding 1 ml of 4% APCD solution. APCD was freshly synthesized in this laboratory because it decomposes gradually upon exposure to light. Sample solution was transferred into a 50-ml volumetric flask, 5 ml of MIBK was added, and the mixture was shaken vigorously for 1 min. The MIBK layer was lifted to the neck of the flask by addition of deionized water. A series of standard solutions was prepared in the same way. Atomic absorption is measured by aspirating MIBK solution into the air-acetylene flame.

A sampling boat was also used for lead determination. Up to 1 ml of sample solution was introduced into the boat and dried by being placed close to the flame. The boat and the residue were pushed into the flame after the drying and the signal was recorded as a peak. The peak areas of all samples were measured as an estimation of the amounts of lead present.

The graphite furnace was used for determination of lead in the second half of the work. The sample solution was diluted from 1 to 10. A series of standards was prepared ranging from 0 to 0.05 ppm. Operating conditions of the furnace are given in Table 2.

Table 2. GRAPHITE FURNACE CONDITIONS FOR LEAD

	Time, s	Temperature, °C
Drying	50	150
Ashing	50	400
Atomizing	3	2500

6. Cadmium

Cadmium line 228.8 nm was used in this work. The graphite furnace was employed for cadmium determination. The sample solution was diluted from 1 to 100. A series of standard solutions was prepared containing from 0.001 to 0.005 ppm of cadmium. Operating conditions are given in Table 3.

Table 3. GRAPHITE FURNACE CONDITIONS FOR CADMIUM

	Time, s	Temperature, °C
Drying	50	150
Ashing	50	400
Atomizing	5	2400

7. Arsenic

Arsenic line 193.7 nm was used in this work. The sample solution was diluted from 1 to 10, and a series of standard solutions was prepared containing 0 to 0.15 ppm of arsenic. Operating conditions for the graphite furnace are given in Table 4.

Table 4. GRAPHITE FURNACE CONDITIONS FOR ARSENIC

	Time, s	Temperature, °C
Drying	50	150
Ashing	50	400
Atomizing	3	2300

8. Antimony

Antimony line 231.2 nm was used. The sample solutions were diluted a hundredfold and a series of standards ranging from 0 to 0.003 ppm of antimony was prepared. Operating conditions for the graphite furnace are given in Table 5.

Table 5. GRAPHITE FURNACE CONDITIONS FOR ANTIMONY

	Time, s	Temperature, °C
Drying	50	150
Ashing	50	400
Atomizing	3	2400

9. Selenium

Selenium line 196.0 nm was used. Standard addition methods were used to offset the matrix effect, which becomes pronounced when sample solution is used without substantial dilution. The sample solutions were mixed with equal portions of standards containing 0, 0.05, 0.10, and 0.15 ppm of selenium. Operating conditions of the graphite furnace are given in Table 6.

Table 6. GRAPHITE FURNACE CONDITIONS FOR SELENIUM

	Time, s	Temperature, °C
Drying	60	180
Ashing	70	450
Atomizing	4	2400

10. Tellurium

Tellurium line 214.3 nm was used. For the same reason as for selenium, standard addition methods were used. A series of standard solutions containing 0 to 0.15 ppm of tellurium was added to the samples. Operating conditions of the graphite furnace are given in Table 7.

Table 7. GRAPHITE FURNACE CONDITIONS FOR TELLURIUM

	Time, s	Temperature, °C
Drying	60	180
Ashing	70	450
Atomizing	5	2400

11. Mercury

Mercury line 253.7 nm was used. A Perkin-Elmer mercury analysis system was assembled with the Perkin-Elmer atomic absorption spectrophotometer Model 303 for mercury determination. The reducing agents used were 5% hydroxylamine and 10% stannous chloride. The method was checked according to reference materials of the National Bureau of Standards and found to be reliable. A 100-ml aliquot of each sample solution was taken for each determination. A standard curve was prepared by use of 50 and 100 ng of mercury.

CHAPTER II. RESULTS AND CONCLUSIONS

A. PROXIMATE AND ULTIMATE ANALYSES

Table 8 gives the proximate and ultimate analyses of the samples. It was expected that the volatile materials decrease as the percentage of ash increases throughout the gasification process. However, the reverse happened at Runs R-FP-147 and F-OH-9, and R-OH-9 and F-EGO-37, which should have identical values on the table. This indicates some difficulties with the homogeneity of the samples, and resulted in an increase in concentration of beryllium, vanadium, and chromium in the samples between the feed and residue stages of pretreatment. This increase is illustrated by the values of beryllium in Figure 8 and for chromium and vanadium in Figure 9, referenced later in the paper.

B. ASHING OF COAL

The relationship between RF power input and sample temperatures is shown in Table 9.

To discover the effect of the sample particle size on the rate of oxidation, samples were used in a series of new experiments under the same ashing conditions as before except that the samples were unground and contained on the average of 90% by weight of –8 to +80 mesh size fractions.

A comparison of the results indicates that for partially gasified coal and char residues, the particle size of crushed coal below 8 mesh size has little or no effect on the rate of low-temperature ashing, but –8 to +80 raw coal samples require up to 60 hours for ashing as compared with 30 hours for a similar raw coal passing an 80 mesh screen. The ashing times versus the percentages of ash for various –80 mesh samples are shown in Figures 2 through 7.

Based on the values of Table 9 and the desirability of keeping the LTA ashing temperature as low as possible while still keeping the ashing time to a minimum, we have arrived at the following schedule.

Oven-dried coal samples are initially placed in the 6-cell LTA and oxidized

Table 8. PROXIMATE AND ULTIMATE ANALYSES, wt %

Proximate, As Rec'd	F-FP-147	R-FP-147	F-OH-9	R-OH-9	F-EGO-37	R-EGO-37
	wt %					
Moisture	1.4	3.7	3.1	0.8	1.6	0.2
Volatile Matter	38.6	22.4	22.4	2.2	2.6	2.1
Ash	11.6	12.3	11.1	22.1	20.9	45.0
Fixed Carbon	48.4	61.6	63.4	74.9	74.9	52.7
Total	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate, Dry Basis						
Ash	11.73	12.76	11.48	22.24	21.23	45.04
Carbon	71.0	68.4	69.3	73.8	75.0	53.2
Hydrogen	5.06	3.01	3.32	1.20	1.17	0.61
Sulfur	4.75	3.36	3.88	2.64	2.35	1.56
Oxygen	6.33	11.10	10.75	--	--	--
Nitrogen	1.13	1.37	1.27	0.60	0.59	0.25
Total	100.00	100.00	100.00	100.48	100.34	100.66

Table 9. SAMPLE TEMPERATURE VERSUS POWER INPUT

Power Input, W/cell	Sample Temperature, °C
10	95
15	110
20	125
25	150
30	190

at 10 W/cell for the first 12 hours. The wattage is then increased to 15 W/cell for the next 10 hours, followed by a final oxidation at 20 W/cell until the sample reaches a constant weight. This accounts for a total elapsed time of 30 hours in the LTA.

Our experience with LTA indicates that the ashing is speeded up if the sample is taken out and well mixed once every 2-3 hours during the 30-hour ashing operation; otherwise, the ashing time may be twice as long as when periodic sample mixing is used.

Figures 2 through 7 were prepared from the data based on LTA ashing of six analysis samples, each in duplicate. They clearly indicate that the bulk of the organic matter in coal is oxidized during the first 20 hours and that the oxidation of the remaining 2 or 3% of carbonaceous matter then proceeds very slowly, approaching the complete oxidation line asymptotically. The residual organic matter from this method of ashing does not seem to interfere in the acid dissolution of the samples because, in practice, the sample solution is started with nitric acid followed by perchloric acid, which completely oxidizes any residual carbonaceous matter in the ash samples.

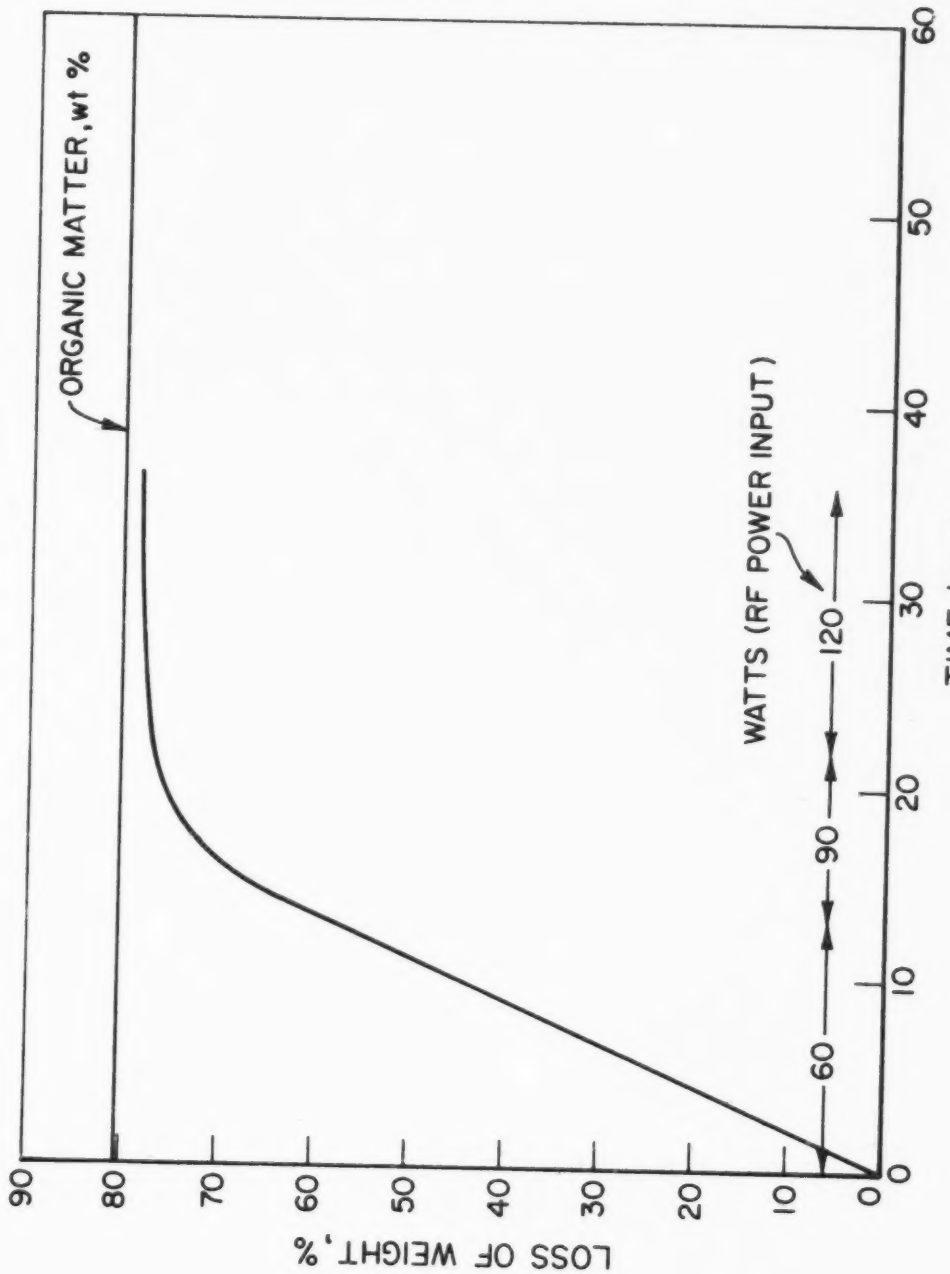

Figure 2. LTA ASHING OF −80 MESH SAMPLES OF F-FP-137

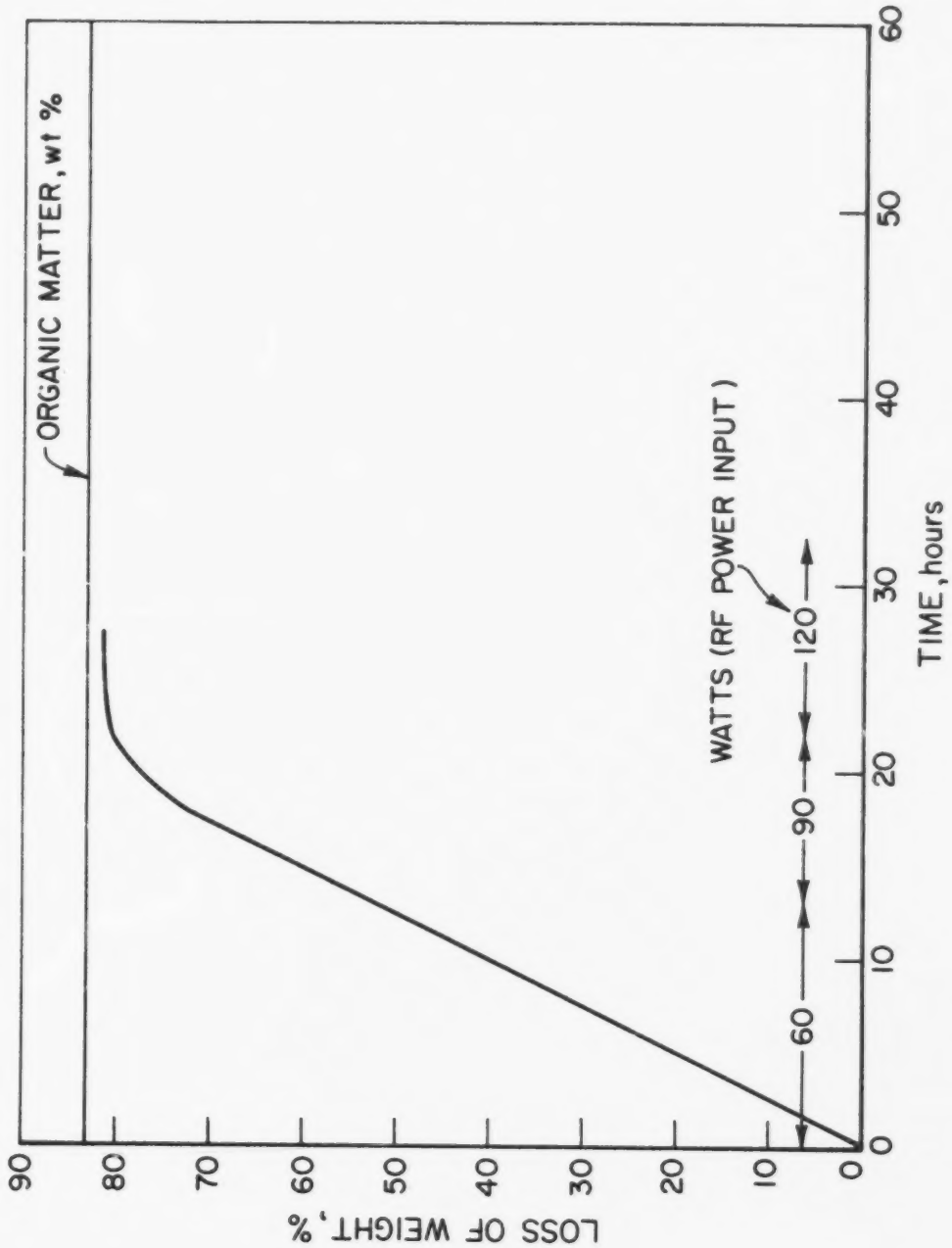

Figure 3. LTA ASHING OF −80 MESH SAMPLE OF F-HTEG-4

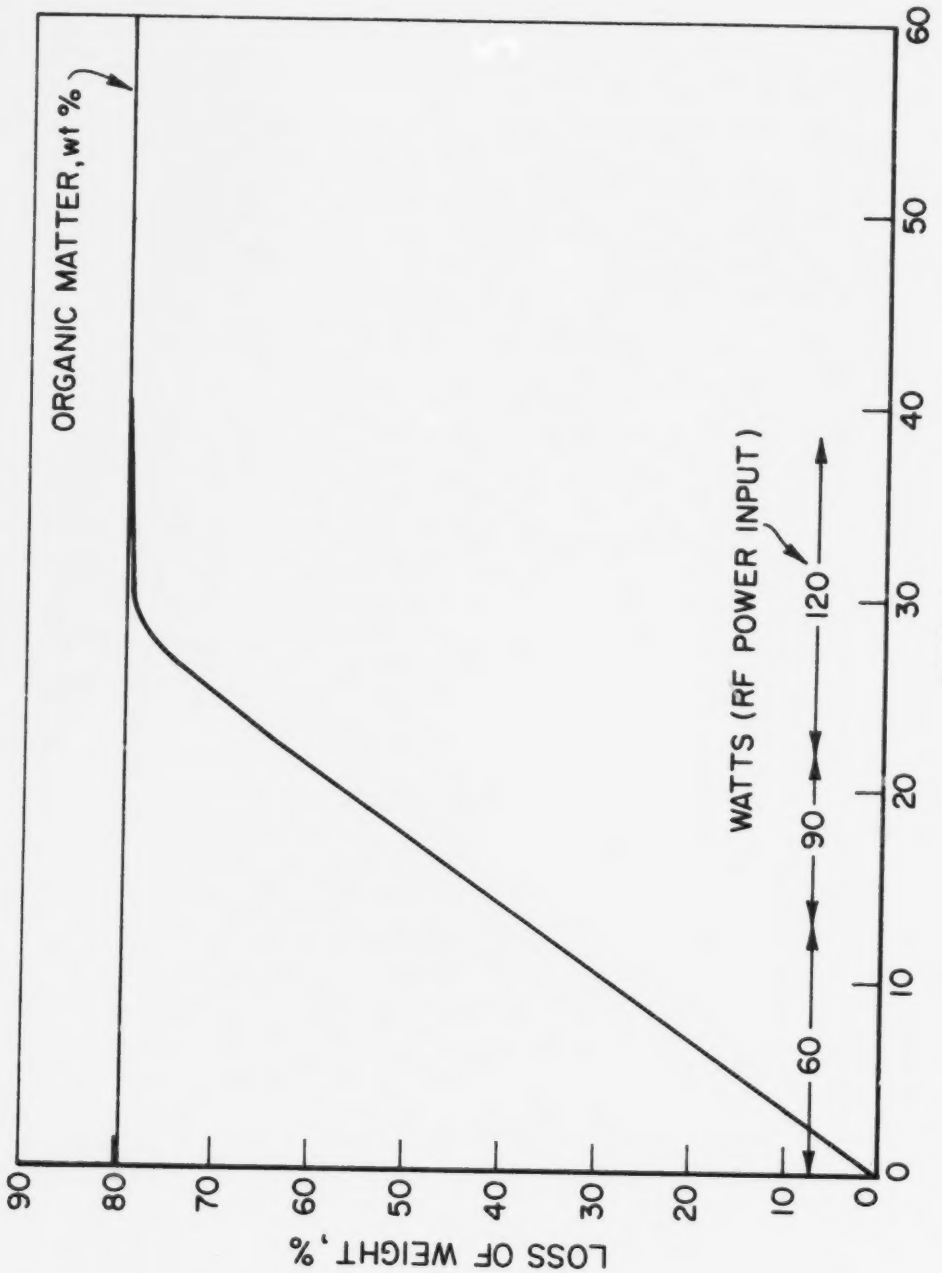

Figure 4. LTA ASHING OF −80 MESH SAMPLE OF F-EG-10

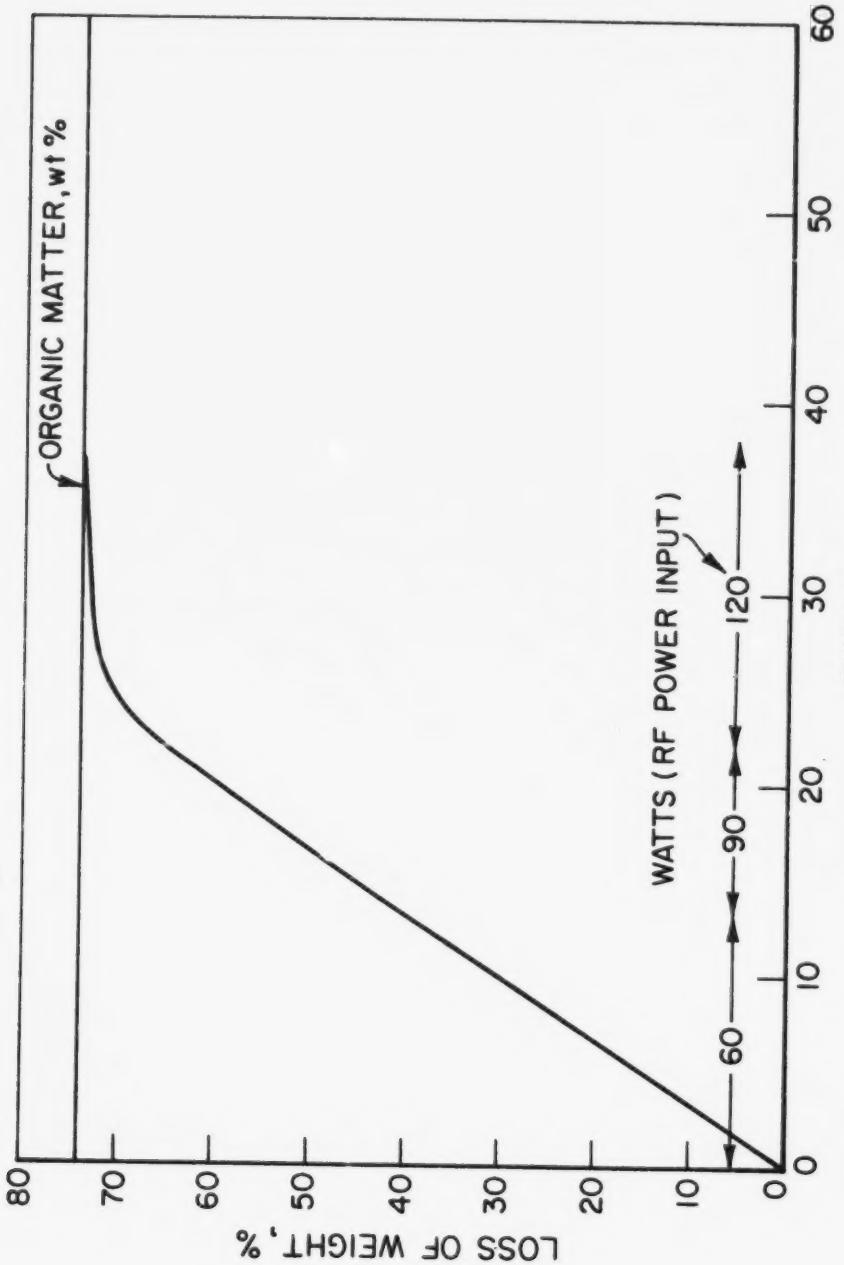

Figure 5. LTA ASHING OF −80 MESH SAMPLE OF R-EG-10

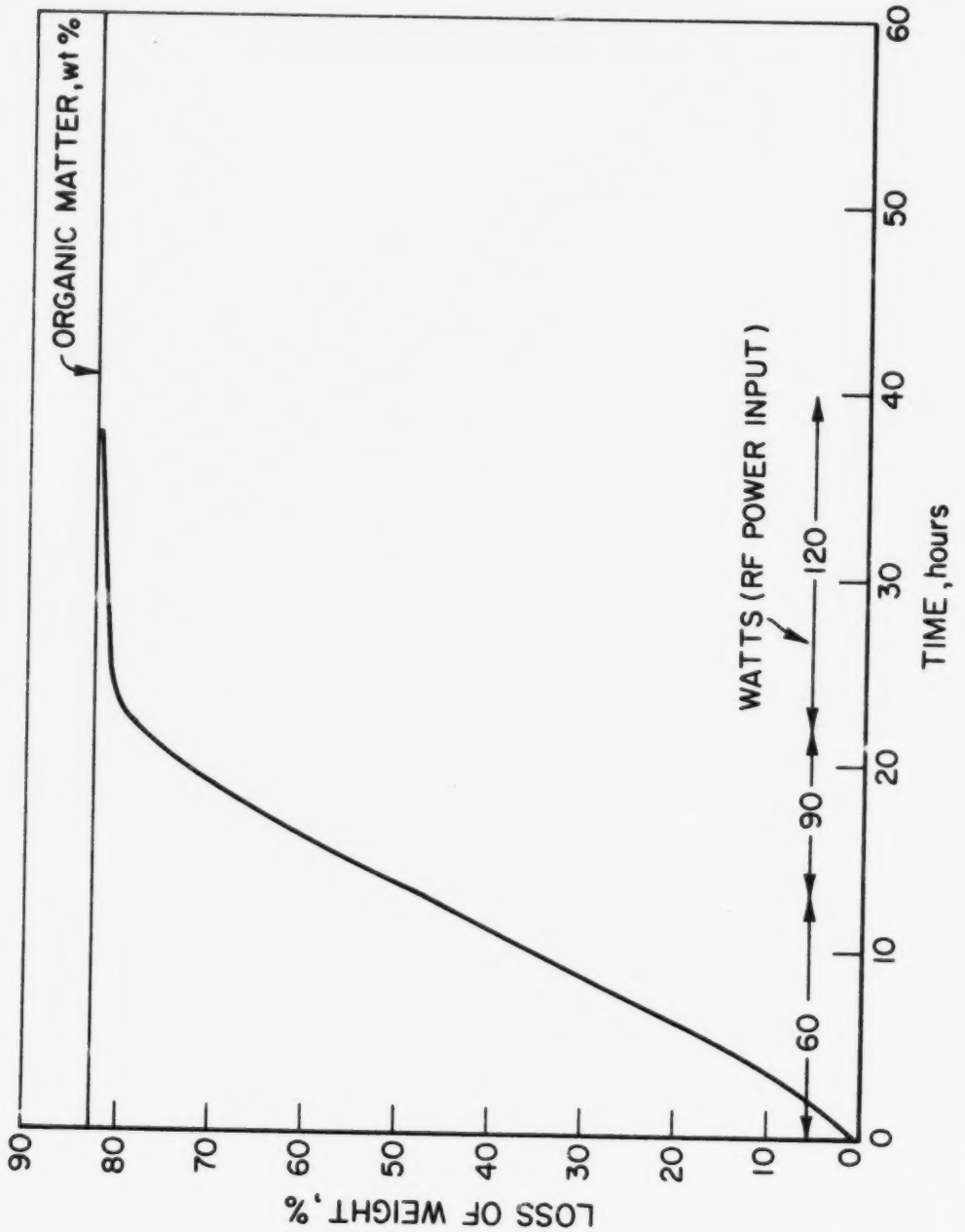

Figure 6. LTA ASHING OF -80 MESH SAMPLE OF F-EG-11

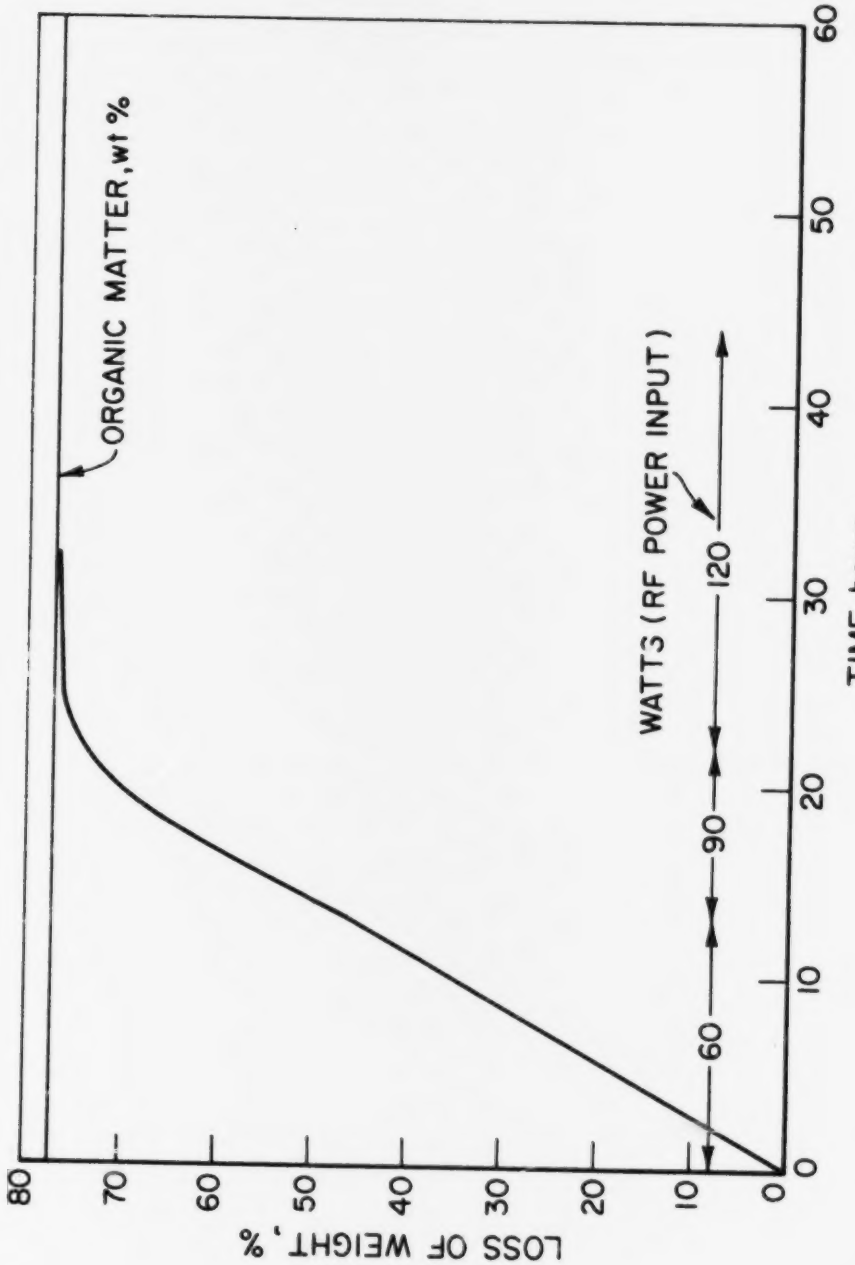

Figure 7. LTA ASHING OF −80 MESH SAMPLE OF R-EG-11

C. DETERMINATION OF INDIVIDUAL ELEMENTS

1. Chromium

Chromium was a relatively easy element to determine in coal samples. Precision of the overall analytical methods, based on six separate analyses of the Ireland mine coal, indicates a relative standard deviation of 1.1% at the concentration of approximately 30 ppm in coal. The analytical results are summarized in Table 10 along with other trace elements.

Table 10. TRACE ELEMENT CONCENTRATION OF PITTSBURGH NO. 8 BITUMINOUS COAL AT VARIOUS STAGES OF GASIFICATION, CALCULATED ON THE RAW COAL (F-FP-147) BASIS

Elements	F-FP-147	R-FP-147, F-OH-9	R-OH-9, F-EGO-37	R-EGO-37	Total Loss, %
	ppm				
Hg	0.27	0.19	0.06	0.01	96
Se	1.7	1.0	0.65	0.44	74
As	9.6	7.5	5.1	3.4	65
Te	0.11	0.07	0.05	0.04	64
Pb	5.9	4.4	3.3	2.2	63
Cd	0.78	0.59	0.41	0.30	62
Sb	0.15	0.13	0.12	0.10	33
V	33	36	30	23	30
Ni	12	11	10	9.1	24
Be	0.92	1.0	0.94	0.75	18
Cr	15	17	16	15	0

With a little variation in its level, chromium is essentially totally retained in the residue throughout the gasification process.

2. Nickel

Determination of nickel at the level of approximately 20 ppm in the Ireland mine coal gave a relative standard deviation of 3.6%, which is reasonably good for this purpose. The analytical results are summarized in Table 10.

During the gasification process about one-fourth of the nickel is lost.

3. Vanadium

Vanadium was determined by nitrous oxide-acetylene flame on the AAS. Five-tenths gram of sample-ash dissolved in a final solution made up to

50 ml gave a vanadium concentration of approximately 2 ppm. The detection limit of the vanadium under the experimental conditions was about 0.7 ppm, with a relative standard deviation of 9% at the 2-ppm level. The results of the analyses are summarized in Table 10 and discussed in Chapter III.

There was a vanadium loss during the gasification process of 30%.

4. Beryllium

Beryllium is a very toxic element. The detection limit of beryllium by the AAS is very low; however, its level in coal is very low also. The beryllium in these six samples was determined both by direct aspiration and by use of a graphite furnace. Both results are shown in Table 11. The standard deviation in the determination of beryllium by the flame method was about 9%. The graphite furnace was used only to check the flame method; therefore, no standard deviation measurement was made. The values reported in Table 10 came from the flame method.

Beryllium showed a loss of 18% during gasification.

Table 11. COMPARISON RESULTS OF BERYLLIUM BY DIRECT ASPIRATION FLAME AND BY GRAPHITE AAS

	Flame	Graphite Furnace
	Be, ppm, calculated on sample basis	
F-FP-147	0.9	0.9
R-FP-147	1.1	0.8
F-OH-9	1.1	0.8
R-OH-9	1.9	1.0
F-EGO-37	1.6	1.0
R-EGO-37	2.9	1.7

5. Lead

Lead was determined by the APCD-MIBK extraction method, the microsampling boat technique, and the graphite furnace. A comparison of the results by these three methods is shown in Table 12 and discussed in Chapter III.

The standard deviation for this method was about 4%. The microsampling boat technique and the graphite furnace were used only to check if the results given by extraction were reasonable. The results from the extraction-flame method are reported in Table 10.

Table 12. COMPARISON RESULTS OF LEAD BY APCD-MIBK EXTRACTION, MICROSAMPLING BOAT, AND GRAPHITE FURNACE

	APCD-MIBK Extraction	Sampling Boat	Graphite Furnace
	—Pb, ppm, calculated on sample basis —		
F-FP-147	5.9	--	5.5
R-FP-147	4.7	4.9	4.6
F-OH-9	4.4	--	4.4
R-OH-9	6.6	7.4	5.5
F-EGO-37	5.7	6.1	5.5
R-EGO-37	8.5	6.6	7.3

Approximately 60% of the lead was lost during the gasification process.

6. Cadmium

The levels of cadmium in the samples were too low to be determined by flame AAS; therefore, the graphite furnace was used. The results are shown in Table 10. The standard deviation for the determination of cadmium was about 6%.

Sixty-two percent of the cadmium was lost during the gasification process.

7. Arsenic, Antimony, Selenium, and Tellurium

These four elements were difficult to determine in the samples, even by use of the graphite furnace. Certain matrix effects, which suppress the signals given by these elements, were shown in the determination. Standard addition methods were used; the results are summarized in Table 10.

These four elements are considered as highly volatile. In this study, loss ranged from 33% for antimony to 74% for selenium.

8. Mercury

Mercury was determined by the cool vapor AAS. A NBS coal standard reference material (SRM) was analyzed along with the samples. The certified value for the SRM is 0.132 ppm. The mercury found by this method was

0.133 ppm, averaged from six runs with a relative standard deviation of 11%. The analytical results are shown in Table 10.

Mercury, a highly volatile element, has a loss of 96% during the gasification process.

CHAPTER III. DISCUSSION

A. THE CHANGE IN CONCENTRATION OF TRACE ELEMENTS AT VARIOUS STAGES OF GASIFICATION

The changes in concentration of trace elements in the coal samples at various stages of gasification are shown in Figure 8. The figure clearly shows the loss of certain kinds of trace constituents from the residue during gasification. However, since there are many other effluents and streams in the gasification process besides the solid residue and the synthetic natural gas, we cannot conclude where these trace elements have gone. More statistical data on the solid residue and also more work on the other kinds of effluents are needed to come to a conclusion as to the fate of these potentially hazardous trace constituents during coal gasification.

B. ANALYTICAL METHODS

1. Flame Atomic Absorption

The flame method is, in general, simple, fast, and relatively free from interferences. However, its sensitivity did not always meet the requirements of this work. Chromium, nickel, and lead were determined by the nitrous oxide-acetylene flame method. The relative standard deviation estimated for chromium was 1.1%, which is very good; nickel was 3.6%, which is fair. As for lead, vanadium, and beryllium, the relative standard deviations were approximately 9%. For lead, the presence of iron made it necessary to use standard addition methods to check the incomplete recovery of lead, which gave the major error in measurements. The major error in measurements for beryllium and vanadium was drifting of the background signal caused by large-scale expansion.

2. Microsampling Assembly

In direct aspirating methods only approximately 10% of the sample can reach the flame. The microsampling assembly is an alternative way to introduce the entire sample into the flame. The sample solution is put in a boat or cup and the solvent is volatilized, then pushed into the flame. By this technique, all the sample elements are volatilized, atomized, and give peak signals at the same time. The nonvolatile residue in the sampling cup and boat and the geometrical configuration of the sampling boat make the

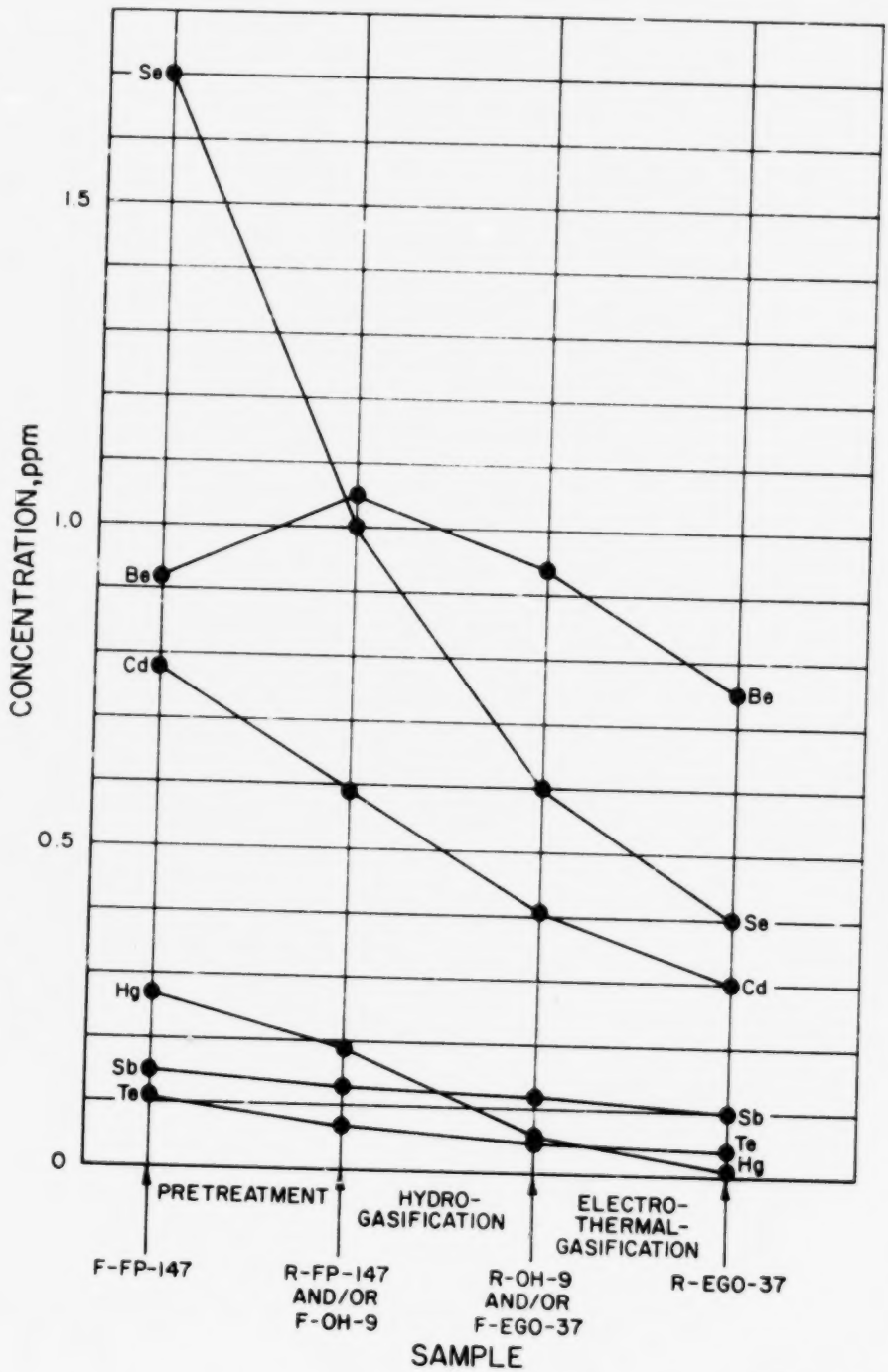

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Figure 8. CONCENTRATION OF TRACE ELEMENTS TESTED IN PITTSBURGH NO. 8 BITUMINOUS COAL (F-FP-147) AND COAL RESIDUES AT VARIOUS STAGES OF GASIFICATION (Part 1. Showing Elements in Low Range of Concentration)

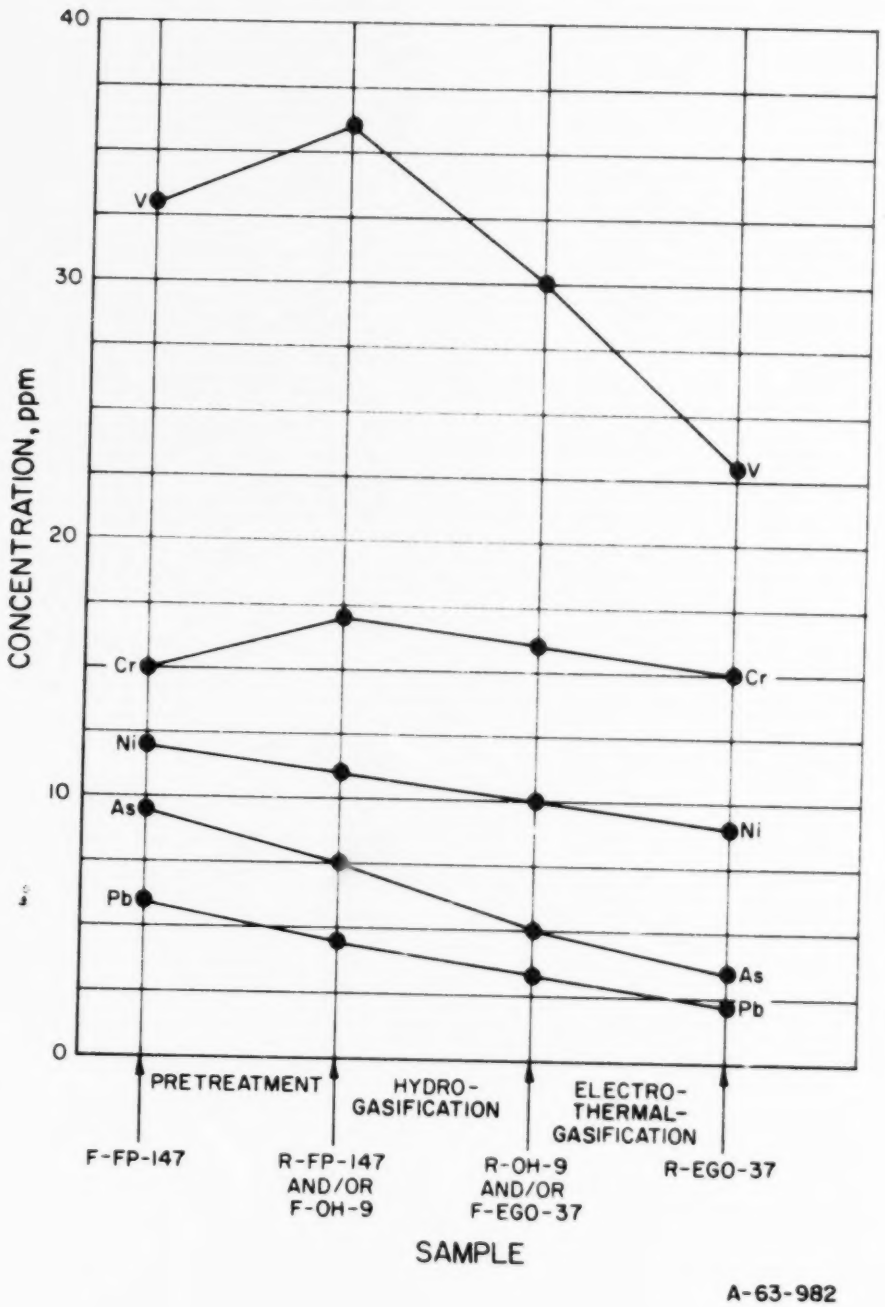

Figure 8. CONCENTRATION OF TRACE ELEMENTS TESTED IN PITTSBURGH NO. 8 BITUMINOUS COAL (F-FP-147) AND COAL RESIDUES AT VARIOUS STAGES OF GASIFICATION (Part 2. Showing Elements in 10-40 ppm Concentration Range)

shape of the peak change from one run to another. Usually, the volatilities of the sample solutions decrease with the increasing amounts of nonvolatile material left in the cup or boat. The peak areas instead of peak heights were measured to eliminate the differences in volatilities of the different samples.

Lead was determined by the sampling boat technique and found to be similar to the extraction method.

3. Graphite Furnace

The graphite furnace has increasingly attracted more and more attention from analytical chemists [11-15]. It increases the residence time of free atoms in optical paths and also creates a very reducing environment which makes possible a higher efficiency in free atom formation processes. Most of the elements give on the order of 10^4 to 10^6 times higher absolute sensitivities when compared with the flame method, and some elements give even higher sensitivities. However, generally speaking, the graphite furnace also has more severe interferences than the flame methods. Very careful work has to be done before one method can be checked out for routine use.

The graphite furnace was used for lead and beryllium for checking purposes. It also was used for those elements which are below the detection limit of flame methods, namely, arsenic, cadmium, antimony, selenium, and tellurium. The determinations of arsenic and tellurium were not so good as for the other elements. The precision was decreased because of a high blank for arsenic and a small signal, even at 3X scale expanion, for tellurium.

The precision was fairly good for beryllium, lead, antimony, and selenium. The relative standard deviations for these elements at the levels measured were all about 3-4%.

4. Mercury Analysis System

The mercury analysis system includes a plastic absorption cell which is placed in the optical path on a Perkin-Elmer 303 atomic absorption spectrophotometer, an aerator fitted into a biochemical oxygen demand bottle, and a pump that circulates the air in the system.

The major error in the mercury determinations is found in the sample preparation step, which was carried out by burning the samples in a C-H train,then collecting them by use of 1% potassium permanganate in 0.1N sulfuric acid.

REFERENCES CITED

1. Belcher, C. B. and Brooks, K. A., Anal. Chim. Acta 29, 202 (1963).
2. Dinnin, J., Anal. Chem. 32, 1475 (1960).
3. Obermiller, E. L. and Freedman, R. W., Fuel 44, 199 (1965).
4. Abernethy, R. F., and Gibson, F. H., Report of Investigation 7184. U. S. Bureau of Mines, 1968.
5. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I., Applied Inorganic Analysis, 2nd Ed. New York: John Wiley, 1955.
6. O'Gorman, J. V., Suhr, N. H. and Walker, P. L., Jr., Appl. Spec. 26, 44 (1972).
7. Bailey, B. W. and Lo, F. C., JAOAC 54, 1447 (1971).
8. Southworth, B. C., Hodecker, J. H. and Fleischer, K. D., Anal. Chem. 30, 1153 (1958).
9. Joensuu, O. I., Appl. Spec.25, 526 (1971).
10. Marineko, J., May, I. and Dinnin, J. I., U. S. Geol. Survey Prof. Paper 800-B, B151 (1972).
11. L'Vov, B. V., Spectrochim. Acta 17, 761 (1961).
12. L'Vov, B. V., Spectrochim. Acta 24B, 53 (1969).
13. Massmann, H., Z. Anal. Chem. 225, 203 (1967).
14. Massmann, H., Spectrochim. Acta 23B, 665 (1968).
15. Woodriff, R. and Ramelow, G., Spectrochim. Acta 23B, 665 (1968).